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CARBOTHERMAL REDUCTION OF UO_3 : INFLUENCE OF THE MIXTURE OF UO_3 AND CARBON POWDERS AND KINETIC MODELLING OF THE REACTION

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Abstract

The influence of the physical mixture of carbon and uranium trioxide powders on the carbothermal reduction of UO_3 has been studied : the texture of the powders mixtures was characterised, and its effect on the reduction into UO_2 was shown. Finally, a kinetic modelling of the carbothermal reduction of U_3O_8 was proposed.

1. INTRODUCTION

Reduction of uranium trioxide by carbon was carried out in order to obtain uranium dioxide, intermediate commonly used in the fabrication process of nuclear combustible. According to the literature[1], the carboreduction of UO_3 to UO_2 involves two steps: the conversion of UO_3 into U_3O_8 and then the reduction by carbon of U_3O_8 into UO_2. Nevertheless, the mechanism for the reduction of U_3O_8 into UO_2 is not clear yet[2-4]. Consequently, our aims were to investigate the effect of the physical mixture of UO_3 and carbon powders on the reduction, and to propose a kinetic modelling for the transformation.

2. EXPERIMENTAL

Two mixtures (UO_3+3C) were prepared using β-UO_3 and carbon. β-UO_3 is obtained from thermal decomposition of ammonium diuranate. A first mixture (UO_3+3C) is obtained by mixing UO_3 with carbon during two hours in a C/U=3 molar ratio; it is then stocked under argon. A second mixture, denoted (UO_3+3C)*, was prepared by a slight manual grinding of the initial mixture, in a mortar until an homogeneous black colour was obtained all over the mixture.
The specific surface area and pore volume were determined from the adsorption and desorption isotherms (BET and BJH methods), using a MICROMERITICS ASAP 2000 apparatus. X-ray powder diffraction spectra were recorded at room temperature on a SIEMENS D5000 diffractometer using nickel filtered Cu-Ka radiation.
Thermogravimetry (TG) experiments were carried out with a SETARAM TAG24 thermal analyser, under flowing gas (2L/h) at atmospheric pressure. The gases evolved during the reactions were simultaneously analysed by a mass spectrometer (BALZERS QMG 120).

3. STRUCTURAL AND TEXTURAL CHARACTERIZATION

The specific surface areas and pore volumes measured for the various powders are reported in Table 1.

Table 1 : Specific surface area and porosity

	C	UO_3	(UO_3+3C)	(UO_3+3C)*
Specific surface area (m^2/g)	98.5	24.6	32.2	31.8
Pore volume (cm^3/g)	0.36	0.054	0.1	0.18

The two mixtures exhibit the same specific surface area, but the pore size distributions are different, as shown in Figure 1. The ground mixture exhibits the bimodal porosity due to UO_3 and a large pore distribution centred around 60nm. These new pores can not be attributed to carbon, since their volume and their size are too large compared with those measured on the carbon powder. SEM observations[5] show that the initial (UO_3+3C) mixture contains large agglomerates (diameter : 200µm), whereas the ground mixture is composed with smaller particles (10µm to 40µm).

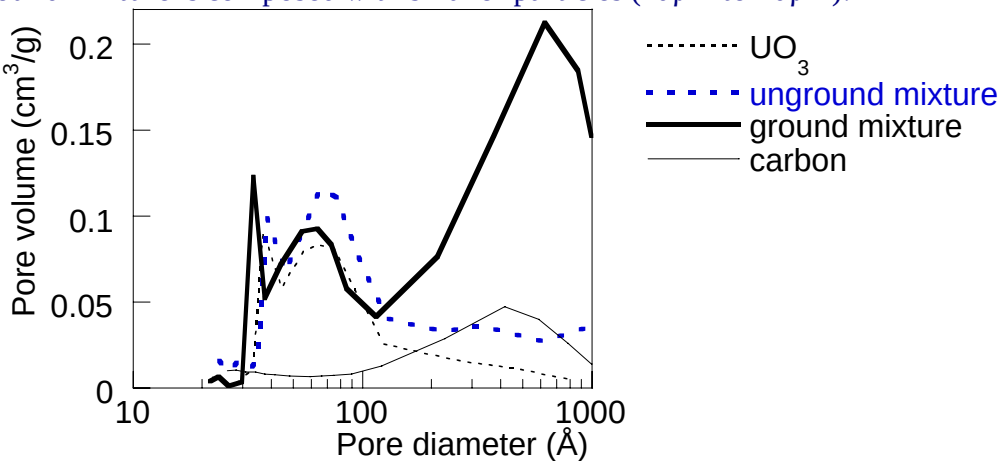

FIGURE 1 : Pore size distributions of the various samples

Consequently, the two mixtures can be represented as follows : the 200µm-agglomerates of the (UO_3+3C) mixture are constituted with smaller aggregates (10µm), the large agglomerates being covered with carbon. The grinding has broken these agglomerates, so that the (UO_3+3C)* mixture contains new agglomerates (30-40µm) of the previous aggregates (10µm), responsible for the new pores (60nm) observed on the ground mixture. The grinding has also improved the contacts between UO_3 and C, carbon being probably better dispersed inside the 40µm-agglomerates.

4. THERMOGRAVIMETRIC STUDY OF THE REACTIVITY OF THE MIXTURES

The mass loss (TG) and the rate of mass loss (DTG) for the unground and ground mixtures heated up to 1200K, under flowing helium, are given on figure 2, as well as the evolved gases observed by mass spectrometry.

The first DTG peak at 373K, observed for both compounds, corresponds to a desorption of water (also observed on the β-UO_3 powder[(5)]). For all the other DTG peaks, carbon dioxide is evolved and, in a smaller extent, nitrogen dioxide (which is due to the way of synthesis of β-UO_3). For the unground mixture, the DTG peak at 823K is characteristic of the thermal decomposition of UO_3 into U_3O_8, as shown elsewhere[(5)]. The other two peaks at 713K and 863K are also observed on the ground mixture, but correspond to higher weight losses in that case.

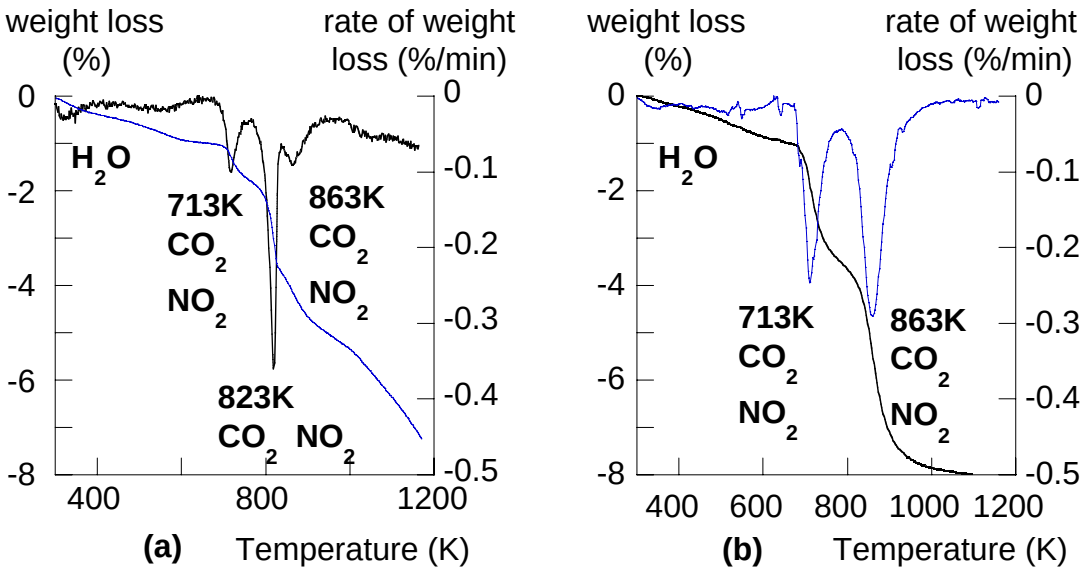

*FIGURE 2 : Curves of weight loss and rate of weight loss for the unground **(a)** and ground **(b)** mixtures, and released gases.*

Moreover, we can notice that the transformation of the ground mixture is completed at 1073K.

The experimental weight loss (2.3%) observed for the ground mixture at 713K corresponds to the theoretical weight loss of the reduction of UO_3 into U_3O_8 by carbon :

$$3(UO_3 + 3C) = U_3O_8 + 1/2\ CO_2 + 17/2\ C \qquad (1)$$

and the 4.6% weight loss observed at 863K corresponds to the reduction of U_3O_8 into UO_2

$$U_3O_8 + 17/2\ C = 3\ UO_2 + CO_2 + 15/2\ C \qquad (2)$$

Besides, X-ray diffraction experiments have confirmed that U_3O_8 only is obtained at 823K and UO_2 at 1173K. Thus, the DTG peaks observed on the two mixtures can be accounted for as follows : reduction of UO_3 by carbon at 713K (it is partial for the unground mixture where only a few carbon grains are in contact with UO_3), thermal decomposition of the unreacted part of UO_3 into U_3O_8 at 823K, carbothermal reduction of U_3O_8 into UO_2 at 863K (the small weight loss observed on the unground mixture corresponding to the part of U_3O_8 grains in contact with carbon).

5. KINETIC STUDY OF THE U_3O_8 CARBOTHERMAL REDUCTION

The kinetic study of the carbothermal reduction of U_3O_8 has been carried out using the ground mixture, in isothermal conditions (550°C, heating rate: 10°C/min), under a flowing gaseous mixture of helium and carbon dioxide (P_{CO2}=5066 Pa). A weight loss curve is given on figure 3. It has been verified that the oxide obtained when the temperature reaches 550°C is mainly U_3O_8 (only a very small proportion of UO_2 is observed). However, the mass loss obtained after 40 hours at 550°C is greater than the theoretical one, and is still continuing.

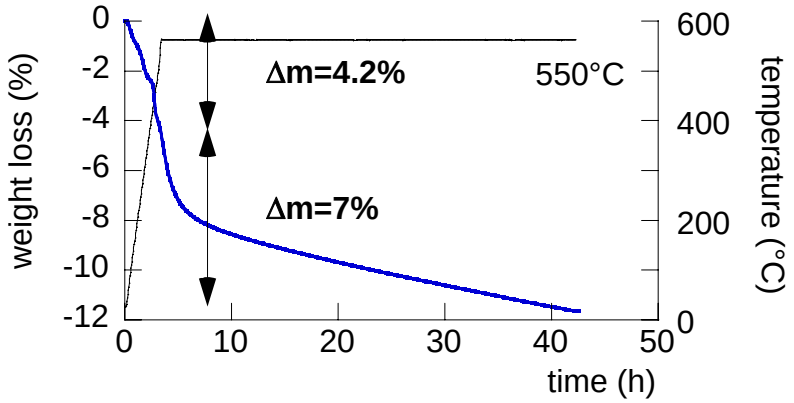

FIGURE 3 : Weight loss curve of the ground mixture at 550°C.

Samples calcined during various duration were analysed by X-ray diffraction: it has been shown that when the mass loss in isothermal conditions is smaller than the theoretical one (4.66%), UO_2 is formed according to the reaction (2). But, for greater mass losses, UO_2 is reoxidized into U_3O_8 by residual oxygen present in the thermoanalyser (the oxygen partial pressure corresponding to the equilibrium between UO_2 and U_3O_8 is about 10^{-7} Pa at 550°C).
Moreover, due to residual oxygen, a parallel reaction of consumption of carbon occurs:

$$C + O_2 = CO_2 \qquad (3)$$

Consequently, the kinetic study was limited to the first two hours of calcination (UO_2 formation), the weight loss resulting from both the reactions (2) and (3).
It has been shown, using a method based on the isolation method[6], that the rate of weight loss can be written as :

$$\frac{d(\Delta m)}{dt} = (a_1\Phi_1 + a_2\Phi_2)E \qquad (4)$$

where Φ_1 and Φ_2 are the rates per unit area ($m^2.mol^{-1}$) of the two parallel reactions (2) and (3) respectively, and E is the extent of the reaction area where the growth limiting step occurs. Equation (4) means that both the growth mechanism of UO_2 and the reaction between carbon and gaseous oxygen have their limiting step on the same reaction area.
Besides, it has been shown that there is no competition between the nucleation and the growth of the UO_2 phase, so that the nucleation step is considered as instantaneous.
Thus, the reaction area where the rate limiting steps of both reactions (2) and (3) occur can be either the surface of carbon or the surface of U_3O_8 grains (neither a diffusion nor an internal interface limiting step can be assumed, since no carbon can be present inside the growing UO_2 layer).
If the reaction area is the carbon surface (carbon is consumed by gaseous oxygen and by oxygen ions diffusing rapidly from the surface of the UO_2 layer to the carbon surface), the extent of the reaction area, E_c, varies with time according to equation (5) :

$$E_c = 4\pi r_0^2 (1 - \frac{V_c}{r_0} vt)^2 \qquad (5)$$

where V_c is the molar volume of carbon, v is the sum of the reactivities Φ_1 and Φ_2 (both reactions contributing to the carbon consumption) and r_0 is the carbon grains initial radius.
If the reaction area is the U_3O_8 surface, it is given by equation (6) :

$$E_{U_3O_8} = 4\pi r_0^2 (1-(z-1)\frac{V_u}{r_0} vt)^2 \qquad (6)$$

where V_U is the molar volume of U_3O_8, v is equal to Φ_1 (only reaction (2) contributes to the consumption of U_3O_8 grains), r_0 is the initial radius of U_3O_8 grains, and z is the ratio of the molar volumes of UO_2 and U_3O_8.
Equations (5) and (6) lead to the same variation of the rate with time, which is in correct agreement with the experimental curves of rate of weight loss versus time. In order to identify the reaction area, it is worth noticing that the function E is proportional, in both cases, to the initial surface area of the considered solid, and thus the rate of weight loss should be proportional to the initial specific surface area of C or U_3O_8. Consequently, two mixtures were prepared using U_3O_8 powders obtained by calcination in air of β-UO_3 during 12 hours ($2 m^2.g^{-1}$) and 4 hours ($5 m^2.g^{-1}$). The curves of rate of weight loss versus time show that the mixture which contains an U_3O_8 oxide having a surface area 2.5 time higher than the other one do not lead to a higher rate in the same ratio.
Consequently, the reaction area where the rate limiting steps of the parallel reactions (2) and (3) occur is the surface of the carbon grains.

6. CONCLUSIONS

From texture characterisations and thermogravimetry experiments, it has been seen that the carbothermal reduction of uranium oxide greatly depends on the quality of the mixture of the powders. Besides, the isothermal kinetic study of the transformation of U_3O_8 into UO_2 has shown that two parallel reactions occur: the reduction of U_3O_8 and the carbon oxidation. A typical feature is that these two reactions have their rate-limiting step in the same reaction area: the surface of carbon grains.
Finally, it has been observed that for long reduction times, UO_2 is reoxidized into U_3O_8 by reaction with residual gaseous oxygen.

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